Method of Reducing Thick Film Stress of Spin-On Dielectric and the Resulting Sandwich Dielectric Structure

FIELD OF THE INVENTION

5   The present invention relates to a semiconductor manufacturing process, and in particular to a method of reducing thick film stress of a spin-on dielectric and the resulting sandwich dielectric structure.

BACKGROUND OF THE INVENTION

10   Spin-on dielectric layers have been widely used to meet the planarization requirement, preventing a depth focus problem from occurring in the succeeding lithography process, and thus the accuracy of photo-patterning is improved. The planarization of spin-on dielectric layer in general requires a thick dielectric layer to be spin coated, while the stress of the dielectric layer is increased with the increment of the spin coating thickness. A spin-on dielectric layer will crack if its thickness/stress is too large, resulting in a high leaking current, and thus the dielectric layer loses the insulation characteristic. In order to avoid these drawbacks, a dielectric material was spin coated twice to obtain a thicker dielectric layer. Further, a dielectric layer having a low dielectric constant in general suffers a poor thermal stability and anti-water penetration ability, and thus there is a need to develop a technique to form a dielectric layer having enhanced properties.

    US Patent No. 6,294,832 discloses a semiconductor device having a structure of copper interconnect/barrier dielectric liner/low-K dielectric trench and its fabrication method, in which a barrier dielectric liner made of a nitrogen-containing liquid-phase-deposition (LPD) fluorosilicate glass (FSG) film is used to replace a barrier metal layer and an oxide liner.

SUMMARY OF THE INVENTION

30   The present invention provides a technique to reduce a stress of thick spin-on dielectric layer by forming a sandwich dielectric structure, wherein a first

dielectric layer is formed on a substrate by spin coating, a liquid phase deposited (LPD) fluorosilicate glass (FSG) layer is formed the first dielectric layer, and a second dielectric layer is formed on the LPD silica layer by spin coating. The LPD silica layer can be further subjected to a nitrogen plasma treatment so that

5   the whole FSG film is nitridized to prevent movable ions from penetrating through, and enhance thermal stability and anti-water migration ability in effectiveness, and thus the reliability of the spin-on dielectric layer can be improved greatly. As a result, the spin-on dielectric layer will have a higher potential in more applications.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross sectional schematic view of a conventional methyl silsesquioxane (MSQ) dielectric layer prepared by a double spin coating method.

Fig. 2 is a cross sectional schematic view of a thick sandwich dielectric

15   layer prepared by the method of the present invention.

Fig. 3 shows the stress of the layers at different steps of the methods according to Examples 1 and 2 of the present invention and Control Example 1.

Fig. 4(a) shows ESCA spectra of N 1s for LPD FSG films with/without nitrogen plasma treatment.

20   Fig. 4(b) shows ESCA spectra of Si 2p for LPD FSG films with/without nitrogen plasma treatment.

Fig. 5 shows nitrogen concentration depth profiles of LPD FSG film with/without nitrogen plasma treatment by ESCA.

25   ## DETAILED DESCRIPTION OF THE INVENTION

The present invention discloses a method for reducing thick film stress of spin-on dielectric comprising the following steps:

a) spin coating a first dielectric layer on a substrate;

b) growing a liquid-phase-deposition (LPD) silica layer on the first

30   dielectric layer; and

c) spin coating a second dielectric layer on the LPD silica layer.

Furthermore, the present invention discloses a sandwich dielectric structure having a reduced thick film stress comprising:

a first dielectric layer having a thickness between 100 to 700 nm formed on a substrate;

5   a liquid-phase-deposition (LPD) silica layer having a thickness between 5 to 100 nm formed on the first dielectric layer; and

a second dielectric layer having a thickness between 100 to 700 nm formed on the liquid phase deposited (LPD) silica layer.

Preferably, the first dielectric layer and the second dielectric layer are a 10   low–K dielectric layer selected from hydrogen silsesquioxane or methyl silsesquioxane (hereinafter abbreviated MSQ). Preferably, the first dielectric layer and the second dielectric layer are methyl silsesquioxane.

Preferably, the liquid-phase-deposition (LPD) silica layer is a fluorine-containing silica layer having 6–10 atom% of fluorine.

15   Preferably, the liquid-phase-deposition (LPD) silica layer is a liquid-phase-deposition (LPD) silica layer subjected to a nitrogen plasma treatment or NH_3 plasma treatment and has 3–50 atom% of nitrogen and 0.5–10 atom% of fluorine.

Preferably, the liquid-phase-deposition (LPD) silica layer has a thickness of 10 to 30 nm.

20   Preferably, the summation of the thickness of the first dielectric layer and the second dielectric layer are between 800 to 1200 nm.

Preferably, the method of the present invention prior to step c) further comprises:

b') thermal curing the resulting substrate/the first dielectric layer/the LPD 25   silica layer structure from step b). More preferably, the thermal curing in step b') is carried out in a nitrogen atmosphere at a temperature ranging from 150 to 650℃ for a period of 30 minutes to 2 hours.

Preferably, the method of the present invention prior to step c) further comprises:

30   b') subjecting the LPD silica layer to a nitrogen plasma treatment or NH_3 plasma treatment. More preferably, the nitrogen plasma and the NH_3 plasma

treatment is carried out under conditions of: 25-400℃, 10-800 mTorr, a RF power density of 0.2-2 W/cm^2, flow rate of nitrogen gas or NH_3 being 100-2000 sccm, and a period of treatment time ranging from 30 sec to 2 hours.

Preferably, step b) of the present invention comprises immersing the
5 substrate into a silica-supersaturated hydrofluosilicic acid (H_2SiF_6) solution to form a fluorine-containing silica layer on the first dielectric layer for a period of time. A suitable method for preparing the silica-supersaturated H_2SiF_6 solution includes elevating a temperature of a silica-saturated H_2SiF_6 solution for 10℃ or above. Preferably, the temperature of the silica-saturated H_2SiF_6 solution is about
10 0℃, and the elevated temperature of the silica-supersaturated H_2SiF_6 solution is about 25℃. A suitable method for preparing the silica-saturated H_2SiF_6 solution includes adding a sufficient amount of silica powder into a H_2SiF_6 solution having a concentration between 0.5-5.0 M, stirring the resulting mixture at 0℃ for a period of time, and then filtering the mixture for removal of undissolved
15 silica powder.

Preferably, the method of the present invention prior to the spin coating of the second dielectric layer in step c) further comprises heating and drying the LPD silica layer grown in step b).

Preferably, the method of the present invention before the thermal curing in
20 step b') further comprises heating and drying the LPD silica layer grown in step b).

Preferably, the method of the present invention before the nitrogen plasma treatment or the NH_3 plasma treatment in step b') further comprises heating and drying the LPD silica layer grown in step b).

25 Preferably, the method of the present invention after the spin coating of the second dielectric layer in step c) further comprises thermal curing the resulting substrate/the first dielectric layer/the LPD silica layer/the second dielectric layer structure from step c). More preferably, this thermal curing is carried out in a nitrogen atmosphere at a temperature ranging from 150 to 650℃ for a period of
30 30 minutes to 2 hours.

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Control Example 1

Fig. 1 shows a double coating structure of the conventional spin-on dielectric, which was prepared by spin coating a MSQ dielectric on a silicon
5　substrate twice, each with a spin-coating thickness of 500 nm, and curing each MSQ dielectric layer in a nitrogen-flowing furnace tube at 400℃ for 30 minutes.

Example 1

To prepare LPD FSG film, 80 g silica powder was first dissolved into 1500
10　ml of 4 M H_2SiF_6 solution at 0℃, and the resulting mixture was stirred for 24 hrs and filtered to removed the undissolved silica·powder and obtain a silica-saturated H_2SiF_6 solution. As the silica-saturated H_2SiF_6 solution was heated in a constant temperature water bath at 25℃, supersaturation of silica occurred. The supersaturation of silica is caused by low solubility of silica in H_2SiF_6 solution at
15　high temperature. The temperature of the constant temperature water bath was the temperature at which the FSG was grown.

MSQ dielectric material was coated on a silicon substrate by spin coating, so that a first MSQ dielectric layer having a thickness of about 500 nm was formed. The resulting substrate/MSQ dielectric layer was immersed into the
20　supersaturated H_2SiF_6 solution at 25℃, and a LPD FSG was grown on the first MSQ dielectric layer to a thickness of about 25 nm. At this temperature, the deposition rate is about 20 nm/hr. The substrate/MSQ dielectric layer/LPD FSG layer structure so formed was removed from the supersaturated H_2SiF_6 solution, baked at 180℃ for one minute and 250℃ for another one minute, and subjected
25　to a first curing treatment (400°C, 30 minutes). A second MSQ dielectric layer was then formed by spin coating followed by a second curing treatment (400℃, 30 minutes), and a structure as shown in Fig. 2 was obtained.

Example 2
30　The procedures of Example 1 were repeated to obtain a substrate/MSQ dielectric layer/LPD FSG layer/MSQ dielectric layer structure, except that the

first curing treatment was omitted.

A thin film stress measuring device (Tencor FLX-2908) was used to measure non-destructively the inner stresses in the layers formed at different steps of the preparation methods for the structures according to Control Example 1, Example
5 1 and Example 2. The measuring device includes a He–Ne laser source, a reflector, lenses, and a positioning sensor. By rotating the reflector, the laser light would scan the surface of the substrate/layer structure. Then the positioning sensor measured the shift of the reflecting light from the surface of the substrate/layer structure, and the curvature of the substrate/layer structure was
10 obtained. The radius of curvatures R_0 and R of the substrate/layer structure before and after the deposition of a layer were measured, respectively. A stress in the thin film (σ) was calculated via the Stoney equation [Stoney 1909]:

$$\sigma = \frac{1}{6}\left(\frac{E_S}{(1-v_S)}\right)\left(\frac{t_s^2}{t_f}\right)\left(\frac{1}{R} - \frac{1}{R_0}\right)$$

where Es, t_s, and v_s are Young's Modulus, thickness and Poisson ration of the
15 substrate, and t_f is the thickness of the thin film. The results are shown in Fig. 3.

It can be found in Fig. 3 that, for Examples 1 and 2 having a LPD-FSG sandwiched between MSQ dielectric layers, the final thin film stresses are 53.9Mpa and 44.4Mpa, respectively, which are significantly lower than 70 MPa of the stress of the double coating structure in Control Example 1. Therefore, the
20 LPD-FSG has an effect of reducing the stress of the thick film.

In another embodiment of the present invention, the LPD FSG layer having a thickness of 25 nm on the first MSQ dielectric layer was placed in a PECVD reactor, where a nitrogen plasma treatment was carried out for a nitridation of the LPD FSG layer under the following conditions: flow rate of N_2 of 200 s.c.c.m;
25 process temperature 200℃; temperature of the upper plate 250℃; RF energy density 1.13 W/cm^2; pressure 400 mTorr; and process time 15 minutes. MSQ material was further spin coated on the LPD-FSG so as to form a sandwich structure of MSQ/LPD FSG/MSQ. Finally, the structure was placed in a furnace tube with a nitrogen flow for curing (400℃, 30 minutes).

30 Fig. 4(a) and 4(b) shows the surface chemical composition and chemical

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shifts of the LPD FSG layers with/without nitrogen plasma treatment by using
Electron Spectroscopy for Chemical Analysis (ESCA). It can be seen from the
spectra of nitrogen atom bonding (N 1s) in Fig. 4(a) that the LPD FSG layer
without nitrogen plasma treatment (represented by the dashed line) does not have

5   any nitrogen bonding therein. On the contrary, the LPD FSG layer with nitrogen
plasma treatment has an intense peak at the binding energy of 397.4 eV, which is
just within N 1s peak position range of 396.97–397.82 eV for SiON film. From
the spectra of silicon atom bond (Si 2p) in Fig. 4(b), it can be seen that the LPD
FSG layer without nitrogen plasma treatment has an intense peak at the binding

10   energy of about 103.4 eV, which is mainly attributed by silicon oxide (SiO_x) bond.
The LPD FSG layer with nitrogen plasma treatment has an intense peak at the
binding energy of about 102.2 eV, which is primarily attributed by SiON bond.
From above it is known that the intense peak of Si 2p spectra of the LPD FSG
layer after the nitrogen plasma treatment is changed from 103.4 eV to 102.2 eV.

15   This is mainly because part of the Si-F bonds and Si-O bonds in the as-grown
layer are changed to Si-N bonds after the nitrogen plasma treatment, wherein
nitrogen atoms permeate into the as-grown layer and replace some of the oxygen
or fluorine atoms therein.   Further, nitrogen atom has an electron affinity
smaller than those of oxygen atom and fluorine atom, therefore the intense peak

20   of Si 2p spectra of the LPD FSG layer with nitrogen plasma treatment shifts
toward a smaller binding energy.

Fig. 5 shows nitrogen concentration depth profiles of LPD FSG layer
with/without nitrogen plasma treatment by ESCA. It can be seen from this figure
that nitrogen atom can be detected along the depth from the surface of the layer to

25   the silicon substrate after the nitrogen plasma treatment, and the density thereof
is maintained above 20 atom%. No nitrogen atom is substantially detected from
the LPD FSG layer without nitrogen plasma treatment, wherein the
concentrations there measured are close to noise values. It can be understood
from the data in Figs. 4 and 5 that nitrogen atom can uniformly penetrate into the

30   LPD FSG layer by subjecting the LPD FSG layer to a nitrogen plasma treatment,
and nitrogen can replace oxygen or fluorine to form N–Si bond. As a result, the

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effect of nitrogen plasma treatment is not restricted to the surface, but a nitridation of the whole layer.

LPD FSG and MSQ dielectric materials are both low–K dielectric materials, and a combination of them can result in a decrease in the stress in the dielectric
5   thick film and a reduce in RC delay thereof.   Furthermore, the defects of high water absorption and poor thermal stability of MSQ film can be improved, and thus the oxidization and even erosion of metal conductive wires can also be improved. Therefore, the present invention has a great potential to be used in many applications in the future semiconductor manufacturing processes.

10   Although the present invention has been described with reference to the preferred embodiments, it will be understood that the invention is not limited to the details described thereof. Various substitutions and modifications have been suggested in the foregoing description, and others will occur to those of ordinary skill in the art. Therefore, all such substitutions and modifications are intended to
15   be embraced within the scope of the invention as defined in the appended claims.